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Langmuir–Blodgett films: molecular engineering of non-centrosymmetric structures for second-order nonlinear optical applications

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Optical second-harmonic generation (SHG) is conditional upon the structure being non-centrosymmetric and consequently, the Langmuir–Blodgett (LB) technique is of interest because it permits control at the molecular level. However, the criteria for alignment at the air/water interface, *i.e.* a hydrophilic head and a hydrophobic tail, tend to impede the required packing arrangement within the multilayer. Most show inversion symmetry with the interfaces being alternately hydrophobic (tail-to-tail) and hydrophilic (head-to-head). This has been overcome by interleaving the layers with inactive spacers and, in such films, the long-range structural order is controlled by utilising compatible component molecules, interdigitating arrangements (*'molecular zips'*) and interlayer hydrogen-bonding. Furthermore, the employment of optically nonlinear chromophores with two hydrophobic end groups eliminates the need for inactive spacers. The molecules form stable non-centrosymmetric structures because, unlike above, the interfaces are invariably hydrophobic. In this review, the molecular requirements for LB deposition are discussed together with the film-forming behaviour and properties of a variety of optically nonlinear materials.

1. Introduction

Organic materials are highly efficient frequency doublers of the visible and near infrared regions of the spectrum and, in general, have higher optical damage thresholds and larger hyperpolarisabilities (β) than their inorganic counterparts.[1] The molecules should be acentric because second-order effects only occur in media which lack inversion symmetry but, as recently shown,[2,3] this is not a prerequisite as long as the aggregate structure complies. However, large second-order nonlinearities are usually associated with molecules which possess an intramolecular charge transfer axis, *i.e.* donor–(π-bridge)–acceptor materials, the properties being dependent upon the length of the bridge,[4,5] the planarity of the chromophore[6] and the nature of the substituent groups.[7] The hyperpolarisability is enhanced by increasing the conjugation length and there is an optimum combination of donor and acceptor strengths for any π-electron bridge.[8] The requirements have been discussed at length in several reviews[1,9,10] and suitable compounds are readily identifiable from their molecular structures.

The optical nonlinearities of the bulk film or crystal relate to the dependence of the induced polarisation (P) on the higher orders of the electric field (E) of the incident radiation [eqn. (1)].

$$P = \varepsilon_o\{\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 \ldots\} \qquad (1)$$

The $\chi^{(n)}$ terms correspond to the first, second and third-order susceptibilities and, in the absence of a significant intermolecular contribution, for example, resulting from charge transfer, the bulk values are attributable to the tensor sum of the individual molecular components (α, β and γ) corrected for orientation and local field effects. The structure must be non-centrosymmetric for SHG and other even-order effects but, as the nonlinearity (β) is optimised when the molecule is dipolar, the natural antiparallel alignment must be constrained.

Donor–(π-bridge)–acceptor molecules tend to adopt a centrosymmetric arrangement which causes the susceptibility to be cancelled in the bulk. This may be overcome in a number of ways, for example, by utilising molecular chirality[11] or by alignment in an applied electric field above the glass transition temperature.[12] LB deposition is also recognised as an important technique for obtaining films with the required structure (Fig. 1). It permits amphiphilic molecules, those with a hydrophilic head and a hydrophobic tail, to be aligned at the air/water interface and allows the structure of the deposited film to be controlled. Most adopt a centrosymmetric head-to-head and tail-to-tail arrangement but a few, *e.g.* 2-docosylamino-5-nitropyridine (DCANP)[13] and its derivatives,[14–19] display non-centrosymmetric herringbone arrangements and

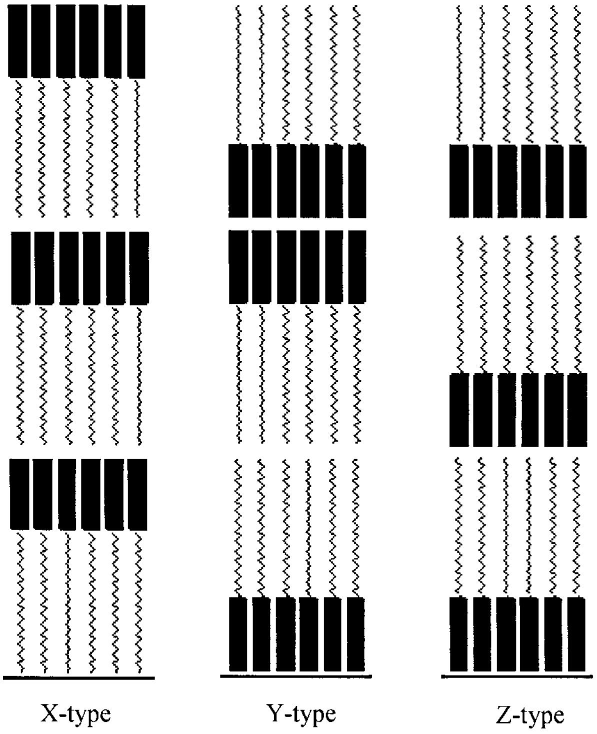


Fig. 1 Schematic representation of centrosymmetric (Y-type) and non-centrosymmetric (Z-type and X-type) LB film structures, the latter differing only in the orientation of the molecules with respect to the substrate.

are SHG-active. For most other compounds it is necessary to alternate the optically active layers with inactive spacers but few have exhibited the expected quadratic SHG dependence to thicknesses in excess of 100 bilayers.[20–27] They include interdigitating arrangements ('molecular zips'),[20,21] all-polymeric films[23,24] and examples where carboxylic groups on adjacent layers hydrogen-bond and enforce long-range order.[27] In controlling the structure, as above, the optically nonlinear chromophores are diluted by the inactive spacers and the SHG is reduced to 25% of the optimum value if all layers were SHG-active and appropriately aligned. However, the spacer may be omitted and non-centrosymmetric alignment retained if both ends of the chromophore are hydrophobic.[28] This invariably results in Z-type arrangements and recent studies have resulted in a quadratic dependence of the second-harmonic intensity to thicknesses suitable for waveguiding.[28–34]

Pitt and Walpita[35] first established that LB multilayers could be used as planar waveguides and, since then, there have been several reports of guiding in SHG-active films[36–46] including LB overlays evanescently coupled to monomode[47] and multimode[48] optical fibres. However, with the exception of DCANP,[36–41] which has a non-centrosymmetric herringbone structure, the majority of studies has concerned alternate-layer LB structures.[42–45] The results are promising but, for such films, the second-order properties are attenuated by the inactive spacer layers. Thus, the quest for non-centrosymmetric films, which exclude the spacers but which show the expected quadratic SHG enhancement, is of considerable importance.

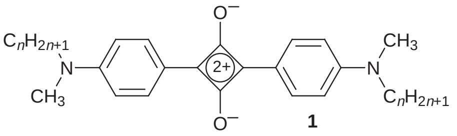
In this article, LB film structures of optically nonlinear dyes and methods for controlling the molecular alignment are reviewed. As the molecules tend to adopt a Y-type arrangement, which is usually centrosymmetric, it is necessary to manipulate the molecular structure so as to favour the alternative film types. Attempts to impose non-centrosymmetric arrangements (X-type or Z-type) on conventional materials usually result in the molecules inverting to a Y-type configuration during, or shortly after, deposition. Thus, to overcome the problem, it is necessary for opposing ends of the molecules to be compatible when adjacent in the multilayer film.[28] Alternatively, if the terminal group of the chromophore is charged, Coulomb repulsion may be utilised to suppress a head-to-head bilayer arrangement.[49,50] In addition, as recently demonstrated, centrosymmetric molecules can give rise to SHG even though their molecular hyperpolarisabilities (β) are effectively zero.[2,3] This arises from the formation of acentric dimers, or higher molecular aggregates, and strong SHG may result if there is a significant intermolecular charge transfer contribution to the bulk second-order susceptibility ($\chi^{(2)}$). Thus, when designing the amphiphilic materials, it may be relevant to sterically hinder any opposing charge transfer interactions at the layer interfaces.

2. LB Deposition

A variety of trough designs is commercially available but the most suitable, for fabricating non-centrosymmetric structures, comprises two compartments separated by a fixed surface barrier on which the substrate carrier and dipper mechanism are situated.[51] The optically nonlinear dyes are spread from an immiscible solvent (*e.g.* $CHCl_3$) onto the pure water subphase of the trough. Then, after evaporation of the solvent, the surface layer is compressed to give a floating monolayer (Langmuir film). Deposition occurs when a substrate is passed through the compressed film and, for optimum ordering of the optically nonlinear chromophores, it is preferable to deposit the SHG-active film on the upstroke and, for alternate-layer structures, the interleaving spacer on the subsequent downstroke. Without the spacer, single-legged materials tend to form centrosymmetric Y-type structures in which the molecular layers pack hydrophilically (head-to-head) and hydrophobically (tail-to-tail) at successive layer boundaries. This may be overcome by utilising molecules with hydrophobic end groups but it is important that they adopt an extended conformation.[28–34] The films are referred to as Z-type, even though one of the hydrophobic groups is adjacent to the substrate, in this case, the category referring to deposition on the upstroke and a non-centrosymmetric structure. In contrast, for conventional materials, the terms X-type and Z-type are used to denote respectively the situations when the aliphatic tail and hydrophilic head are adjacent to the substrate.

3. Aggregation-induced SHG of centric molecules

Prior to the initial discovery of strong SHG from LB films of symmetrically substituted squaraines (*e.g.* $\chi_{\text{eff}}^{(2)} = 250$ pm V^{-1} at 1.064 μm for **1**)[2,3] it was widely assumed that the molecule, as well as the bulk film, must be non-centrosymmetric. However, extensive delocalisation causes the donor (anilino) and acceptor (C_4O_2) groups to be co-planar and, from X-ray crystallographic analysis,[52–54] the molecular dimensions of one half are symmetry generated by the atomic co-ordinates of the other. The first hyperpolarisability (β) is effectively zero and consequently, the second-order properties are inherent to the aggregate rather than the molecule itself. The experimental data for dye **1** and other squaraine derivatives provide justification to dismiss interfacial effects as the cause of the unusual properties: (a) the SHG is too strong[2,3] and comparable with the signal from conventional donor–(π-bridge)–acceptor materials; (b) the optical nonlinearity is maintained when the chromophore layer is separated from the glass substrate by a hydrophobic buffer[55] but is suppressed when the films undergo transitions to an H-aggregate phase;[56] and (c) SHG has been observed from a free-standing solid solution of dye **1** in poly(vinyl acetate).[57] This clearly demonstrates that the properties are not an artefact arising from the underlying substrate. Therefore, to satisfy the structural requirement for LB films and solid solutions, it may be assumed that the molecules of the smallest SHG-active unit, the dimer, adopt an acentric T motif with the donor of one directed towards the central acceptor of the other (Fig. 2).[2,3] This concept has been verified by the theoretical analysis of Brédas and Brouyère[58] and independently corroborated by Honeybourne.[59] Their work provides a theoretical basis for the second-order activity of



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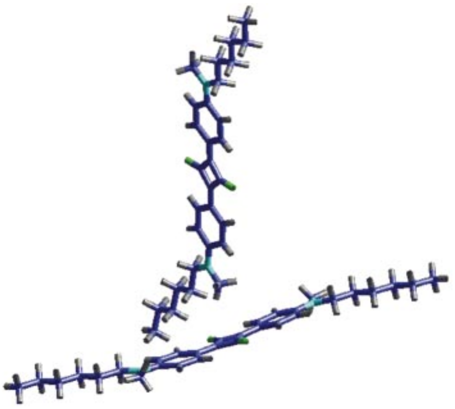


Fig. 2 Simulated arrangement of 2,4-bis[4-(*N*-methyl-*N*-hexylamino)-phenyl]squaraine molecules in an SHG-active dimeric aggregate (Diagram courtesy of J.-L. Brédas and E. Brouyère).

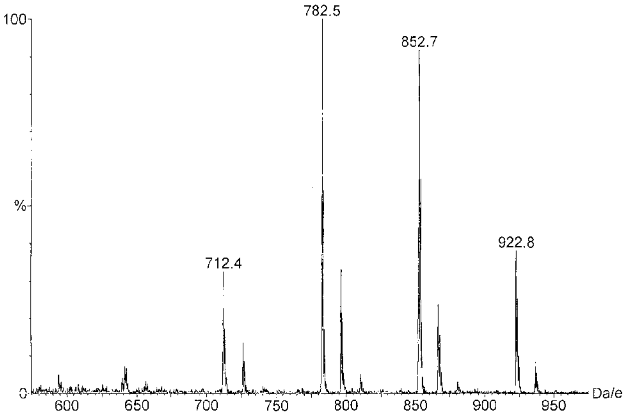


Fig. 3 2,4-Bis[4-(*N*-methyl-*N*-hexylamino)phenyl]squaraine: electrospray ionisation mass spectrum depicting the fragmentation pattern of the dimeric aggregate ($m/z = 923$ $[2M+2H]^+$).

centric molecules and demonstrates that large second-order coefficients can arise from charge-transfer aggregates.

Squaraines readily associate, even in dilute solution, and exist as monomers in aqueous solutions of β-cyclodextrin and as dimers in the larger cavity of the γ-form.[60] When not restricted in this manner, the association number is compound specific and varies from two to seven. The larger aggregates result from hydroxy-substituted derivatives with sterically unhindered dialkylamino groups.[61] However, most form dimeric aggregates[62–64] and their electrospray ionisation mass spectra exhibit peaks with high mass/charge values which conform to $m/z \equiv [2M+nH]^+$ (Fig. 3). The assumption of $z = 1$ is not necessarily appropriate but the uncertainty has been erased by the simultaneous analysis of two different analogues.[64] The mass spectra exhibit the expected aggregate peaks of the separate components and, in addition, a *single* heteromolecular peak conforming to $[M+M'+nH]^+$. Satellite peaks would be expected for higher molecular ratios if z were greater than 1. The aggregates persist in solid solution and, as expected from theory, the second-harmonic intensity from films of **1** increases quadratically with the concentration of dye. However, the SHG is extinguished when electron acceptors are incorporated into the film and this is explained by the fact that competing heteromolecular interactions suppress self association.[57]

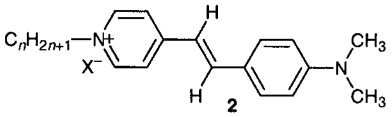
The association number and nonlinear optical properties illustrate a simple structure–property relationship. Dyes that form higher aggregates show no discernible SHG when cast as solid solutions[61] and their arrested crystallites exhibit a blue-shifted absorption maximum. Solid solutions of dyes which form dimeric aggregates tend to be SHG-active and the absorption band of the crystallites is red-shifted relative to the solution spectrum.[3,] The aggregate structure is modified in the LB film but, as a simple indicator, SHG-activity is usually associated with a broad absorption maximum or intense shoulder at 650–730 nm. The dyes are polymorphic and alternative LB phases, albeit SHG-inactive, have sharp absorption bands at *ca.* 520–530 nm (H-aggregate) and *ca.* 750–770 nm (J-aggregate). The former has been assigned to a face-to-face arrangement of chromophores and the latter to a parallel array, with equivalent donor/acceptor overlaps at opposite ends of adjacent molecules.[65] However, many films exhibit phase coexistence and SHG occurs if there is a band or significant shoulder at *ca.* 650 nm.

4. Interlayer charge transfer

The effect of intermolecular interactions on the second-order properties has been mainly overlooked but clearly they have a profound effect. This applies not only to squaraines dyes but also to conventional materials where, for example, calculations which utilise the SHG data (*e.g.* β from $\chi^{(2)}$) may be inappropriate. Intermolecular interactions are also particularly relevant to the design of materials for use in interleaved LB structures where interlayer charge transfer (Fig. 4a) may be exploited to improve long-range structural order as well as the nonlinear optical behaviour. But there are few examples. Bjørnholm *et al.*[66] have reported SHG from the interface between LB layers of 7-(*N*-octadecylaminomethyl)-8,16-dioxadibenzo[*f,j*]perylene (an amphiphilic donor) and 2-octadecylthio-1,4-benzoquinone (an amphiphilic acceptor). The intensity increases quadratically with the number of bilayers but degrades by *ca.* 25% within 15 days. In addition, Neal *et al.*[67] have observed an intermolecular contribution to the susceptibility from the interface between two optically nonlinear dyes, an amphiphilic hemicyanine and 4-heptadecylamido-4′-nitrostilbene. The SHG is improved when the layers pack head-to-head, but not when they pack tail-to-tail, the susceptibility of the head-to-head bilayer being *ca.* 3 times the sum of the nonlinearities of the individual component layers. The response is serendipitous. In interleaved films of complementary molecules, *i.e.* where the hydrophobic tails are attached to the donor (*e.g.* C_nH_{2n+1}-D–π–A) and acceptor (*e.g.* D–π–A-C_nH_{2n+1}), the molecular (D→A) and interlayer (A←D) dipoles are opposed (Fig. 4b):

$$C_nH_{2n+1}\text{-D–}\pi\text{–A} \cdots \text{D–}\pi\text{–A-}C_nH_{2n+1}$$

When the chromophores are more closely matched,[68] as in the interleaved hemicyanine films of **2** and **2′** (C_nH_{2n+1} = octadecyl;



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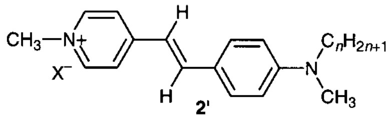
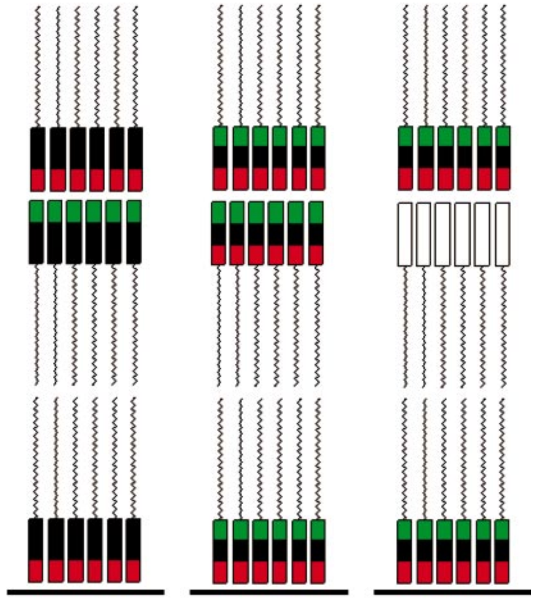


2′



(a) (b) (c)

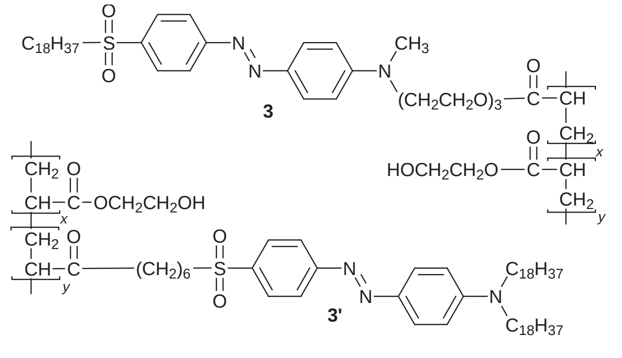
Fig. 4 Schematic representation of alternate-layer films: (a) amphiphilic donors and acceptors; (b) complementary molecules with the tail attached to the donor (C_{2n+1}-D–π–A) and acceptor (D–π–A-C_nH_{2n+1}) in adjacent layers; (c) an optically nonlinear dye and passive spacer. Red, black and green represent the electron donor, π-electron bridge and electron acceptor respectively.

X^- = iodide), the SHG has been found to increase quadratically with thickness but the normalised intensity, $I_{2\omega(N)}/N^2$, where N is the number of bilayers, is reduced compared with the SHG from monolayer films of the individual components: dye **2**, $\chi_{zzz}^{(2)} = 90$ pm V^{-1} at 1.064 μm for $l = 2.9$ nm and $\varphi = 41°$; dye **2′**, $\chi_{zzz}^{(2)} = 145$ pm V^{-1}, $l = 2.5$ nm and $\varphi = 26°$, where l and φ are the layer thickness and chromophore tilt angle, relative to the substrate normal, respectively. The susceptibility of the interleaved film, $\chi_{zzz}^{(2)} = 20$ pm V^{-1}, is modest and significantly higher values have been realised by interleaving the active layers with passive spacers (section 5b).

5. Alternate-layer films

5a. Active–active

As the majority of amphiphilic dyes form centrosymmetric Y-type structures in which the interfaces are alternately hydrophilic (head-to-head) and hydrophobic (tail-to-tail), it is necessary to interleave the SHG-active layers to facilitate an appropriate alignment of the molecular dipoles. This is more readily achieved using passive spacers but may also be carried out using a complementary dye, in this case, with the chromophore hydrophobically substituted at the opposite end (*e.g.* see **2** and **2′**). However, for the susceptibility of the multilayer to equal the sum of the nonlinearities of the two types of component layer, modified by thickness, it is necessary to limit opposing donor–acceptor interactions across the interface. There are few examples[67–76] and, of these, some show a subquadratic SHG dependence with film thickness[69–71] or, if quadratic, have been investigated to only a few bilayers.[72–74] Interestingly, Roberts *et al.*[73] have obtained alternating active layers by the pairwise deposition of two semi-ionomeric polymers, a polycation and a polyanion. In all other cases, the individual layers are deposited separately.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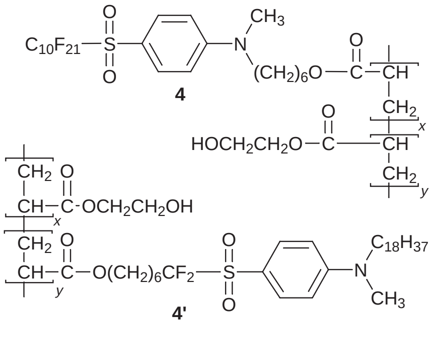
3′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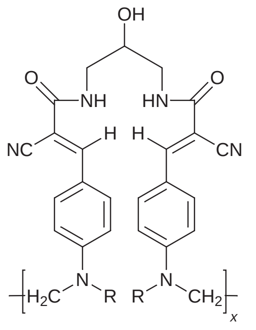
4′

Unlike the examples reported in section 4, Motschmann *et al.*[74] for dyes **3** and **3′** and Wijekoon *et al.*[75] for **4** and **4′** have demonstrated that the bilayer susceptibility is equal to the thickness-modified sum of the individual nonlinearities ($\chi_N^{(2)} + \chi_R^{(2)}$) of the normal and reverse polymers. This suggests that interlayer chromophore interaction is sterically hindered by the polymer backbone in the head-to-head configuration. However, the SHG from alternate-layer films of the former, polymer **3** and reverse polymer **3′**, is constant to only 47 °C and decreases to 35% of the original value when the sample is heated to 68 °C. Another interesting example is the accordion polymer (**5**) and its complementary analogue (**5′**) for which Lindsay *et al.*[76] note that the bridging groups can be functionalised to introduce hydrophobicity, hydrophilicity or hydrogen-bonding. Alternate-layer structures were deposited with transfer ratios of 0.5–0.7 for **5** (R, hexadecyl) on the downstroke and 0.9–1.5 for **5′** (R′, dodecyl) on the upstroke, and the incomplete transfer of **5** may be representative of interdigitating alkyl groups in the adjacent layers.[76] The films exhibit quadratic SHG enhancement to more than 92 bilayers with a second-order susceptibility, d_{33}, of 4 pm V^{-1} at 1.064 μm ($\beta = 6 \times 10^{-39}$ m^4 V^{-1}) and a mean thickness of *ca.* 3.2 nm bilayer^{-1}. A Mach–Zender modulator with an electro-optic coefficient, r_{33}, of 1.1 pm V^{-1} at 890 nm has also been fabricated[76] but unfortunately, the films are unstable with the second-harmonic intensity decreasing to 10% of the original value after *ca.* 2 months at ambient temperature.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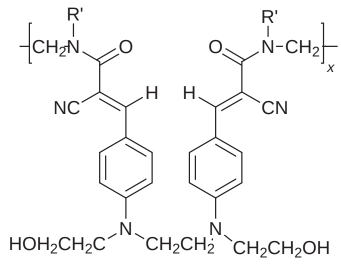
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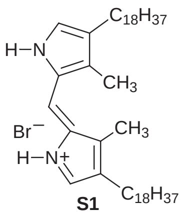
The overall picture of interleaved structures, in which both component layers are SHG-active, suggests that it is difficult to control the film stability[74,76] and long-range structural order.[69–71] Few films have been studied to thicknesses of more than 10 bilayers[75,76] and it may be premature to draw firm conclusions from these limited results. Nonetheless, more interesting data have been obtained from alternate-layer structures in which the second component is passive and, in addition, long-term stability has been reported for Z-type structures of specifically designed materials.

5b. Active–passive

In designing a passive spacer to interleave with the optically nonlinear layers it is necessary to consider the compatibility and deposition characteristics of the components (Fig. 4c). A higher transfer ratio is usually obtained on the upstroke and thus, it is logical to deposit the dye in this direction and the spacer on the subsequent downstroke. It is important to utilise materials that show favourable X-type deposition and, furthermore, which induce long-range order within the multilayer film. This may be achieved by hydrogen-bonding the layers or by interdigitating the hydrophobic tails to retain structural integrity to thicknesses suitable for waveguiding. In addition, for improved behaviour, it is necessary to optimise the molecular characteristics because, as frequently found, minor differences can dramatically affect the deposition, film structure and second-order properties. For example, the hemicyanine dye, (*E*)-4-[2-(4-dimethylaminophenyl)ethenyl]-*N*-alkylpyridinium halide (*e.g.* **2** or **6**), shows improved deposition characteristics when the hydrophobic tail is octadecyl[77] rather than the extensively studied docosyl[78–82] and when the counterion is iodide[77–79] rather than bromide.[80–82] Furthermore, the monolayer susceptibility of **6** ($\chi_{zzz}^{(2)} = 90$ pm V^{-1} at 1.064 μm) is enhanced to *ca.* 500 pm V^{-1} when iodide is replaced by



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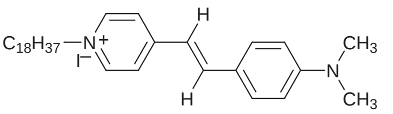

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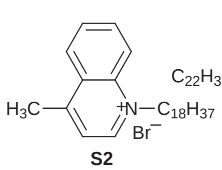

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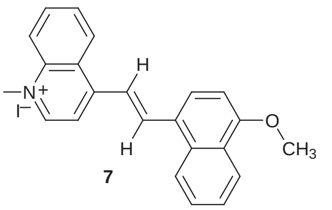

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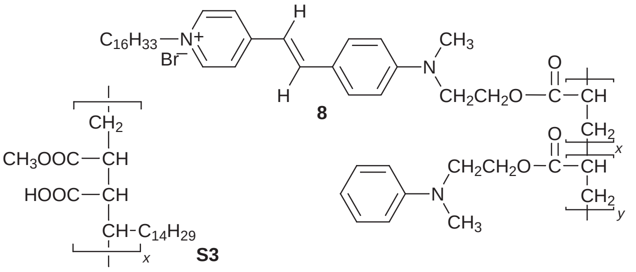
octadecylsulfate.[77] This probably relates to improved alignment when both the cation and anion are amphiphilic, differences in the location of the negative charge relative to the positively charged acceptor, and modified local field effects. However, the high second-order susceptibility has not been obtained for multilayer films.[22]

The first successful attempt[20] to realise quadratic SHG enhancement from an alternate-layer structure of a hemicyanine dye involved **6** and the two-legged spacer, **S1**. The second-harmonic intensity exhibited the expected dependence to 150 bilayers with a susceptibility of $\chi_{zzz}^{(2)}=50\text{–}70$ pm V^{-1} at 1.064 µm, a chromophore tilt angle of 40° and a thickness of 4.7 nm bilayer^{-1}. The spacer was specifically designed to interlock the layers, the cross-section of the hollow between the two legs being taken into account to accept the hydrophobic tail of the optically nonlinear hemicyanine (*i.e.* a 'molecular zip'). Interdigitation is tentatively suggested from the X-ray diffraction data, a *d*-spacing of 4.7 nm being consistent with an interlocking arrangement,[20] but molecular tilt could also account for the reduced thickness. However, evidence of interdigitation has been obtained for alternate-layer films of the wide-bodied dye (**7**) and its spacer (**S2**). They have compatible interlocking geometries and analysis of the films, using surface plasmon resonance (SPR), has yielded thicknesses of 3.18 nm for the dye and 4.29 nm for the bilayer with a tail-to-tail arrangement (*cf.* 4.2±0.1 nm from grazing incidence X-ray synchrotron diffraction).[83] The thickness is significantly less than the combined molecular lengths and, in this case, the diminished depth of the spacer layer, 1.1 nm by subtraction, cannot be rationalised by tilt. Thus, it is assumed that the exposed hydrophobic surface of the dye layer has the appearance of sea grass and that, during deposition, the hydrophobic tails of the spacers interdigitate.

Davis *et al.*[84] have reported an interdigitating Y-type structure for poly(*N*-alkyl-4-vinylpyridinium halide) salts and Ma *et al.*[21] have assumed a similar packing arrangement for alternate-layer films of a hemicyanine dye interleaved with the two-legged spacer, 1,10-bistearyl-4,6,13,15-tetraene-18-nitrogencrown-6, the second-harmonic intensity showing a quadratic dependence to 116 bilayers[21] compared with 30 layers, by the same group, when eicosanoic acid is used as the interleaving component.[85] The latter has a low susceptibility of $\chi_{zzz}^{(2)}=16\text{–}18$ pm V^{-1} at 1.064 µm (*cf.* 50–70 pm V^{-1} for **6** and **S1**)[20] but has been enhanced to 50 pm V^{-1} when poled with an electric field of 1.3 MV m^{-1}. This suggests that the dipoles are aligned by the electric field and that the initially deposited films are structurally disordered.

There have been several related studies on alternate-layer structures of hemicyanine dyes, both monomeric[86–88] and polymeric,[24,89,90] but most have failed to show the theoretically expected SHG enhancement to thicknesses of more than a few bilayers. However, Hodge *et al.*[23] have reported a quadratic

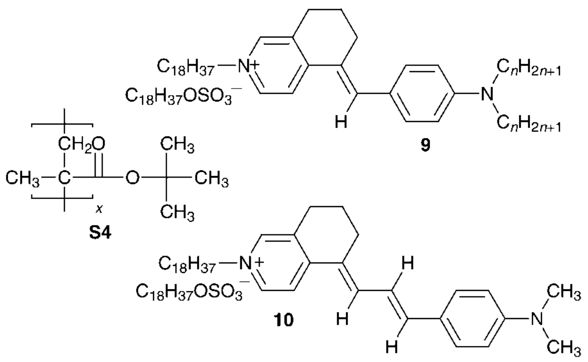


8

S3

dependence to 150 bilayers for dye **8** and the polymeric spacer **S3** and, furthermore, the films have been used to demonstrate an electro-optic Fabry–Pérot modulator.[91] A similar dependence was observed to 300 bilayers with poly(*N*-docosyl-4-vinylpyridinium bromide) as spacer but low effective susceptibilities for this (12 pm V^{-1} at 1.064 µm) and the previous combination (7 pm V^{-1}) suggest an unfavourable alignment of chromophores. In addition, the hemicyanine dyes absorb at the harmonic wavelength with, for example, $A=0.003$ layer^{-1} at 532 nm for dyes **2** and **2′**. Thus, combined with the problems of alignment and the general lack of long-range order within the multilayer, they are not particularly useful as second-order materials.

While retaining the basic molecular structure, the required transparency may be realised by finely tuning the donor/acceptor combination or by sterically hindering the π-electron bridge, thereby causing out of plane rotations of the component groups. This has been achieved for **9**, the LB absorption maxima of the diethylamino to dibutylamino analogues being shifted from 415–435 nm for the pure dye to 440–450 nm when co-deposited in a 1 : 1 ratio with octadecanoic acid (ODA).[34,92] The films exhibit strong SHG and, from its polarisation dependence, the chromophore tilt angle relative to the normal, *i.e.* $\varphi=30\pm1°$, is constant for dye : ODA ratios of 1 : 0 to 1 : 5. The second-harmonic intensity is dependent upon the composition with an optimum susceptibility, *e.g.* $\chi_{zzz}^{(2)}=145$ pm V^{-1} for monolayer films of the diethylamino analogue, arising for the 1 : 1 mixture (Fig. 5). Assuming that the hyperpolarisability is dominated by a single component along the molecular charge transfer axis and that Kleinman symmetry applies, the relation between the bulk ($\chi^{(2)}$) and molecular (β) nonlinearities is given in eqn. (2) and (3).



9

S4

10

$$\chi_{zzz}^{(2)}=Nf^{2\omega}(f^{\omega})^2\beta\cos^3\varphi \tag{2}$$

$$\chi_{zxx}^{(2)}=\tfrac{1}{2}Nf^{2\omega}(f^{\omega})^2\beta\cos\varphi\,\sin^2\varphi \tag{3}$$

N is the number of molecules per unit volume, f^{ω} and $f^{2\omega}$ are local field correction factors at ω (1.064 µm) and 2ω (532 nm) respectively, and $f=(n^2+2)/3$ where n is the refractive index. The apparent variation of the hyperpolarisability is attributed to changes in the local field effects upon dilution with octadecanoic acid (Fig. 5). It is limited when the surface density is

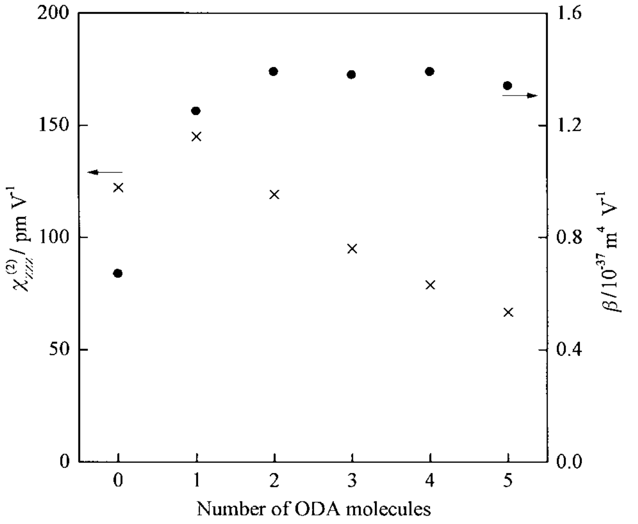


Fig. 5 Variation of the second-order susceptibility ($\chi_{zzz}^{(2)}$) and molecular hyperpolarisability (β) of the diethylamino analogue of dye **9** with the number of molecules of octadecanoic acid associated with the optically nonlinear dye in mixed monolayer films.

high but saturates to a constant value of *ca.* 1.4×10^{-37} m^4 V^{-1} (330×10^{-30} esu) for diluted films of the diethylamino analogue, the behaviour being consistent with the results of Hayden[81] and McGilp *et al.*[93] for related systems.

Dye **9** readily forms non-centrosymmetric LB film structures when interleaved with poly(*tert*-butyl methacrylate) (**S4**) and quadratic SHG enhancement, to more than 100 bilayers, has been realised for each of the dimethylamino to dibutylamino analogues (*e.g.*, see Fig. 6).[92] They are transparent at the fundamental wavelength but have a slight absorbance of 3–5 × 10^{-4} bilayer^{-1} at 532 nm, the values corresponding to a transmittance of 89 to 93% for 100 bilayers compared with 92% for 40 bilayers of DCANP.[37a] Alternate-layer mixed films of the diethylamino analogue and octadecanoic acid (1 : 1 mole ratio), interleaved with poly(*tert*-butyl methacrylate), have an optimum susceptibility of $\chi_{zzz}^{(2)}=67$ pm V^{-1} at 1.064 μm for $l=4.08$ nm bilayer^{-1}, $\varphi=37°$, $n_\omega=1.495$ and $n_{2\omega}=1.581$ respectively. The value is higher than previously obtained for conventional hemicyanine derivatives, even though the absorbance is significantly less, and is enhanced by the nearby charge-transfer band. The efficiency/transparency trade-off is optimised.

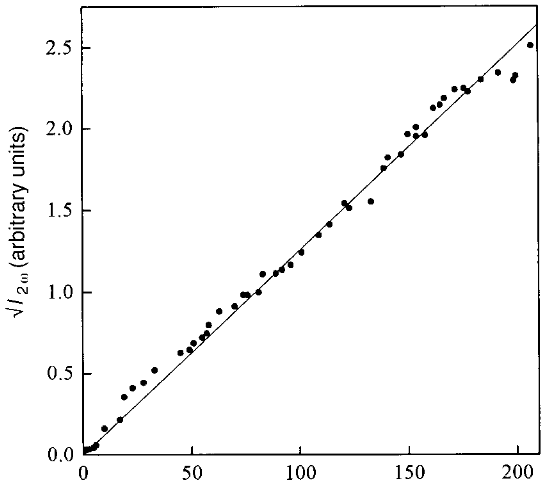
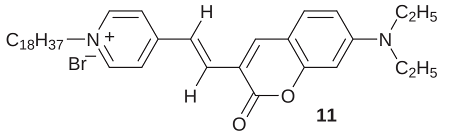


Fig. 6 Typical variation of the square root of the second-harmonic intensity with the number of bilayers of dye **9** and poly(*tert*-butyl methacrylate).

Another interesting example from this group, dye **10** interleaved with poly(*tert*-butyl methacrylate), shows quadratic SHG enhancement to 100 bilayers and the normalised intensity, $I_{2\omega(\mathrm{N})}/\mathrm{N}^2$, where N is the number of bilayers, obtained for the thick LB structures is identical with the monolayer signal.[94] The interleaved films have a susceptibility of $\chi_{zzz}^{(2)}=$ 100 pm V^{-1} at 1.064 μm but, in this case, the extended conjugation causes the absorption band to be red-shifted, with respect to **9**, the absorbance at 532 nm being 0.0015 bilayer^{-1}.



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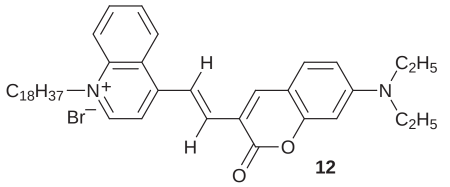

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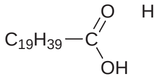
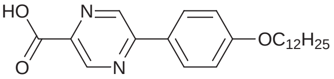
The related coumarin dyes, **11** and **12**, also exhibit quadratic SHG enhancement[95] when interleaved by *N*-docosylquinolin-4-ium bromide (**S2**); they have high effective susceptibilities of 150 and 340 pm V^{-1} respectively, but the values are resonantly enhanced. Interestingly, as described above for the related wide-bodied materials,[83] there is tentative evidence from SPR studies to suggest that the alkyl tails of the dye (**12**) and spacer (**S2**) interdigitate at the hydrophobic interface.[95]

Among other examples of interleaved films, the SHG-active layers include azobenzenes,[96–98] merocyanine dyes,[99] substituted phthalocyanines,[100] organometallic[101] and polymeric[102] derivatives. Most show a deviation from the expected square law dependence for thicknesses less than a few layers and the normalised intensity, $I_{2\omega(\mathrm{N})}/N^2$, is significantly less than the monolayer signal. In spite of this, Era *et al.*[27] have reported excellent film-forming characteristics for an alternate-layer film of a substituted phenylpyrazine (**13**) interleaved with eicosanoic acid (**S5**).



S5



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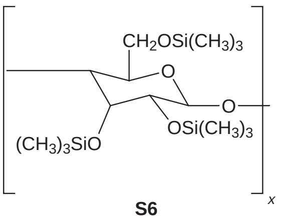
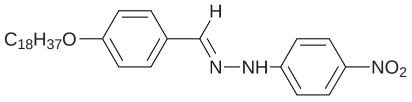
It has a susceptibility of 7 pm V^{-1} at 1.064 μm for a 200 bilayer film, the value being adjusted from that quoted in the original paper using a more recent susceptibility[103] for the reference material. Few films have shown quadratic SHG enhancement to such thicknesses and it may be assumed that long-range order is maintained *via* interlayer hydrogen-bonding when the dye and spacer pack in a head-to-head arrangement.

A similar dependence has been reported for films of a nitrophenylhydrazone (**14**)[44] and a substituted stilbene {dye **15**: R, $\text{-(CH}_2)_n\text{OC(O)C(CH}_3)\text{=CH}_2$},[26] both interleaved with trimethylsilylcellulose (**S6**), the second-order susceptibilities being 19 and 7 pm V^{-1} respectively at 1.064 μm. An optical attenuation of 3.5 dB cm^{-1} at 632.8 nm has been obtained for alternate-layer films of **14** but, at lower wavelengths, the films have an absorbance of *ca.* 7×10^{-4} layer^{-1} at 532 nm. However, with the fundamental propagating in the film and the second-harmonic radiating into the substrate, Hickel *et al.*[44] have observed Cerenkov-type frequency doubling in an LB waveguide using prism coupling. When normalised to 1 W of fundamental power and a 1 cm interaction length, a conversion efficiency of 10^{-8} W^{-1}cm^{-1} was obtained.



S6



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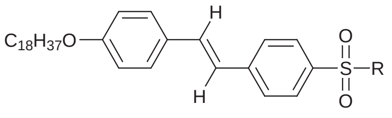

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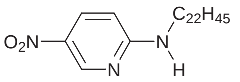
Similarly, using a Cerenkov configuration and end-fire coupling, Penner *et al.*[43] have demonstrated blue (430 nm) and green (532 nm) phase-matched SHG in absorbing waveguide structures of a polymeric azobenzene derivative (**3**) interleaved with poly(*tert*-butyl methacrylate). An optical attenuation of 1 dB cm^{-1} was obtained at 632.8 nm.

As the final example in this section, and probably the most significant, efficient phase-matched blue light generation in a low loss LB waveguide[42] has been achieved by precisely controlling the thickness and modulating the direction of the nonlinear susceptibility. For an alternate-layer LB film of dye **4** and poly(*tert*-butyl methacrylate), comprising two thick adjacent structures with the chromophores aligned in an opposite sense, *i.e.* with their susceptibilities inverted, Penner *et al.*[42a] have reported significant improvement of the overlap integral. This yields a normalised conversion efficiency of 150% W^{-1} cm^{-2} for 819 nm radiation whereas, in films without structural inversion, the second-harmonic intensity is reduced by a factor of 10^3. An optical attenuation of 1.5–2.0 dB cm^{-1} at 457.9 nm and a susceptibility of $\chi_{zzz}^{(2)} = 10$ pm V^{-1} at 860 nm have been reported.

6. Y-Type herringbone arrangements

Most Y-type arrangements are centrosymmetric but, in a few cases, as represented by **16** to **18**, the layers adopt a herringbone arrangement in which the molecular dipoles are aligned in a plane parallel to the substrate (Fig. 7).[13–19] LB films of the octadecyl ($C_{18}H_{37}$) to hexacosyl ($C_{26}H_{53}$) derivatives of dye **16** have bilayer thicknesses of 3.77 to 4.98 nm, from X-ray diffraction, the thickness increasing by *ca.* 0.15 nm per methylene unit.[15] The most extensively studied member of the group, 2-docosylamino-5-nitropyridine (DCANP),[13] has a *d*-spacing of 4.42 ± 0.03 nm and tilt angles, relative to the substrate, of 37 ± 3° for the alkyl tail and 20 ± 8° for the molecular charge transfer axis.[13,15] Non-centrosymmetric alignment of the molecular dipoles, in this case, is probably induced by hydrogen-bonding both within and between layers when the packing is head-to-head. DCANP films are pale yellow ($\lambda_{max} = 374$ nm) and effectively transparent above 500 nm.



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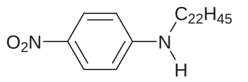

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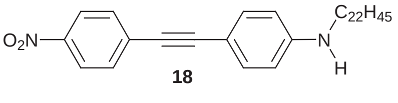

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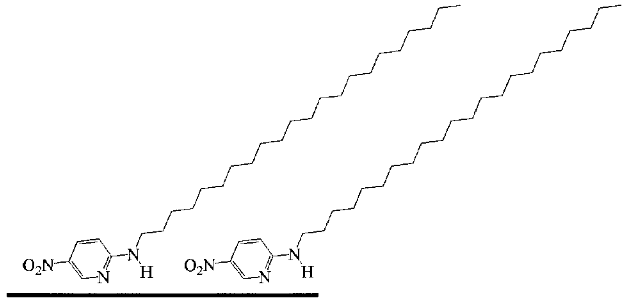


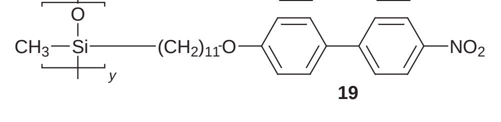
Fig. 7 Schematic alignment of DCANP in the LB monolayer: the molecular dipoles are aligned parallel to the substrate and the alignment is retained in all subsequent layers. The molecules adopt a Y-type herringbone arrangement in the thickness direction.

The second-harmonic intensity increases quadratically with the number of DCANP bilayers. A peak conversion efficiency of 2×10^{-7} was obtained in transmission for a 270 bilayer film (1.2 µm thick), the fundamental intensity and wavelength being 220 MW cm^{-2} and 1.064 µm respectively.[13] Nonlinear susceptibilities of $d_{33} = 7.8 \pm 1.0$ pm V^{-1} and $d_{31} = 2.0 \pm 0.5$ pm V^{-1} at 1.064 µm and a guided wave attenuation coefficient of 12 dB cm^{-1} at 632.8 nm have been reported.[36] The films have been extensively studied as SHG-active waveguides using Cerenkov-type,[37,41] mode conversion,[38,39] and inverted susceptibility configurations.[40,41]

Transparency is not a prerequisite of the Cerenkov-type frequency doubling because the second-harmonic radiation propagates in the substrate and not the film. The efficiency is proportional to the propagation length whereas for mode conversion, *i.e.* a guided fundamental into a guided second-harmonic, the efficiency is proportional to the square of the length. Thus, Cerenkov-type SHG is only more effective when the susceptibility is resonantly enhanced. Bosshard *et al.*[37] have reported a conversion efficiency for DCANP of 4×10^{-4}% W^{-1} cm^{-1} for $\lambda = 820$ nm ($d_{33} = 27$ pm V^{-1}) and 1.4×10^{-7}% W^{-1} cm^{-1} for $\lambda = 1.064$ µm ($d_{33} = 7.8$ pm V^{-1}). At the higher wavelength, Fujiwara *et al.*[41] have reported a 20 to 30 improvement in the Cerenkov phase matched second-harmonic intensity by utilising an inverted susceptibility in the thickness direction. Furthermore, Küpfer *et al.*[40] have obtained a conversion efficiency of 1% W^{-1} cm^{-2} by mode conversion in a $\chi^{(2)}$-inverted LB film structure of DCANP.

7. X-Type films

As deposition is usually better on the up-stroke and, furthermore, because LB layers tend to adopt a centrosymmetric Y-type arrangement, the occurrence of X-type film structures for SHG is rare. However, using the Langmuir–Schaefer technique, a horizontal rather than a vertical deposition method, Lando and co-workers[46] have obtained X-type deposition of a polysiloxane co-polymer (**19**). They reported propagation losses of 2.3 dB cm^{-1} at 800 nm, a thickness of 3.5 nm layer^{-1} from X-ray diffraction, and a first hyperpolarisability of 4×10^{-40} m^4 V^{-1}. The second-harmonic intensity shows a



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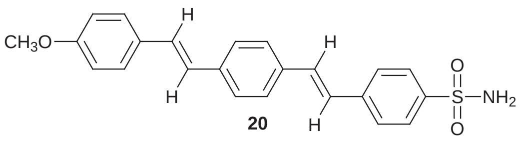
subquadratic dependence to 10 layers with a normalised intensity, $I_{2\omega(10)}/N^2$, equivalent to 12% of the monolayer signal. The intensity continues to increase to 135 layers but with $I_{2\omega(135)}/I_{2\omega(1)} \approx 600$ rather than 1.82×10^4, expected from the square law dependence, the data being obtained from diagrams within the publication. The decay suggests that the film structure is disordered.

Similarly, Aktsipetrov *et al.*[104] have used the Langmuir–Schaefer technique to deposit X-type films of C_{60}-indopane derivatives and, as above, the SHG enhancement is subquadratic. However, X-type LB films of a syndioregic polymer, deposited on the downstroke by vertical rather than horizontal deposition, have exhibited quadratic enhancement to ten layers.[105]

8. Z-Type films

8a. Conventional materials

There have been several claims of Z-type structures but, in many instances, there is confusion between the deposition process and the film type. When deposited only on the upstroke, most materials tend to realign in a head-to-head and tail-to-tail configuration and it is necessary to control the molecular characteristics to stabilise a non-centrosymmetric arrangement. The majority of Z-type films have been studied to less than *ca.* 20 layers. The second-harmonic intensity shows a subquadratic SHG dependence relative to the monolayer signal[106,107] and with increasing thickness.[108–114] This is indicative of the difficulty in controlling the structural integrity of thicker films but, nonetheless, a few examples exhibit the expected behaviour. Aktsipetrov *et al.*[115] have reported quadratic SHG enhancement to 5 layers for an amphiphilic azobenzene dye and Watakabe *et al.,*[116] to 20 layers, for a π-conjugated oligo(phenylenevinylene)sulfonamide (**20**). The latter is unusual in so far as the hydrophobic π-bridge is sufficient to ensure alignment at the air/water interface, its multilayer films having a susceptibility of 9 pm V^{-1} at 1.064 μm, the value being adjusted using a more recent susceptibility[103] for the reference material used. Cheong *et al.*[117] have obtained a quadratic dependence to 40 layers, with $\chi_{zzz}^{(2)} =$ 46.8 pm V^{-1} at 1.064 μm, for a polyamic acid with optically nonlinear 4-nitroazobenzene units. Furthermore, Teerenstra *et al.*[118] have reported corresponding susceptibilities of 3 to 11 pm V^{-1} for 100 layer thick films of poly(isocyanide)s with 2-nitro-4′-dialkylaminoazobenzene side chains, but have not shown the variation with the number of deposited layers.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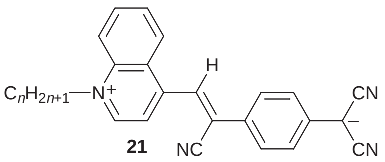
To control the structure it is necessary to introduce features that favour a Z-type arrangement. This may be achieved by using zwitterionic dyes, charged in the terminal position, there being sufficient coulombic repulsion to enforce non-centrosymmetric alignment when the layers attempt to pack head-to-head. Dyes **21** and **22** show a quadratic increase of the second-harmonic intensity with the number of Z-type layers[49,50] and, furthermore, monolayer films of **21** have been used to demonstrate the concept of molecular rectification when sandwiched between metal electrodes.[119,120] However, there is a tendency to adopt an antiparallel arrangement within the layer and films of the long and short tailed derivatives of **21** have very different properties. For example, the hexadecyl analogue has a high susceptibility of 180 pm V^{-1} at 1.064 μm and layer thicknesses of 2.2 nm from SPR[49b] and 2.3 nm from X-ray diffraction.[120] The decyl analogue, albeit shorter, has a thickness of 3.5 nm, from neutron reflection studies on the floating monolayer, and 3.4 nm layer^{-1} from SPR studies on the deposited LB film.[49b] The thickness is greater than the molecular length. Thus, the dipolar molecules probably adopt an antiparallel arrangement within the layer with the decyl tails pointing in opposite directions. This is supported by the fact that the monolayer films exhibit greatly diminished SHG, compared with the signal from hexadecyl analogue, and suggests a tendency towards a centric packing arrangement.[49b]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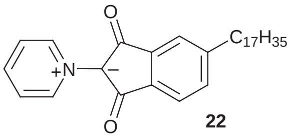
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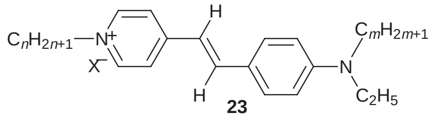
8b. Unconventional two-legged dyes

Ideal molecules, such as fatty acids and their salts, spontaneously organise as monolayers when brought into contact with the water surface and the generally accepted views of the molecular requirements for LB deposition are based on simple amphiphilic materials.[121–123] It is appropriate that the molecules should comprise a hydrophilic group (the head) and one or more hydrophobic groups (the tail) but it is a fallacy that the materials only align with their head groups adjacent to the water surface. Two-legged molecules of general formula:

$$C_nH_{2n+1}\text{-}(D\text{–}\pi\text{–}A)\text{-}C_mH_{2m+1}$$

frequently adopt a stretched conformation,[28–32] albeit in the high-pressure regime of the isotherm, and align with a hydrophobic group, presumably the shorter of the two, adjacent to the subphase. This is corroborated by grazing incidence X-ray synchrotron diffraction studies on floating monolayers, the areas (*e.g.* 0.24 nm^2 for **24**; $m = 22$ and $n = 18$) being consistent with the molecular cross-sections and the data from the pressure-area isotherms.[29b,30] Furthermore, allowing for tilt, the premise is supported by close agreement between the layer thickness and molecular length[30–32] and by the fact that the SHG polarisation dependence demonstrates the chromophores tend to be inclined towards the vertical.[31,32] This conflicts with the popular belief of a U conformation whereby the chromophore would be expected to align parallel to the subphase or substrate. Therefore, at the air/water interface, it may be assumed that repulsion between the aqueous and hydrophobic layers is counteracted by improved van der Waals interactions between more closely packed hydrophobic chains and that the alignment is complicated by other factors such as the energetically favourable conformation of the molecule.

The normalised second-harmonic intensity from films deposited from the upper regions of the isotherms is dependent upon the relative lengths of the two alkyl groups. Optimum values arise when $(m-n)>6$ for **23** and $(m-n)>4$ for **24** but, in both cases, the SHG is suppressed for $m \approx n$ (Fig. 8). This suggests that the dipoles align when the groups are sufficiently different but a random orientation, dipole up and dipole down, occurs when the alkyl groups are similar. The results for **23**, *i.e.* similar intensities on either side of $(m-n)=0$, suggest that the molecular orientation may be controlled by altering the relative lengths of the alkyl chains.[124] Thus, it is feasible to



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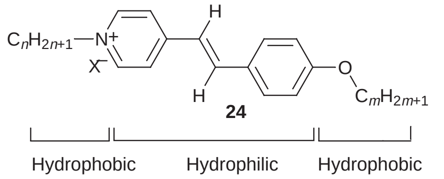

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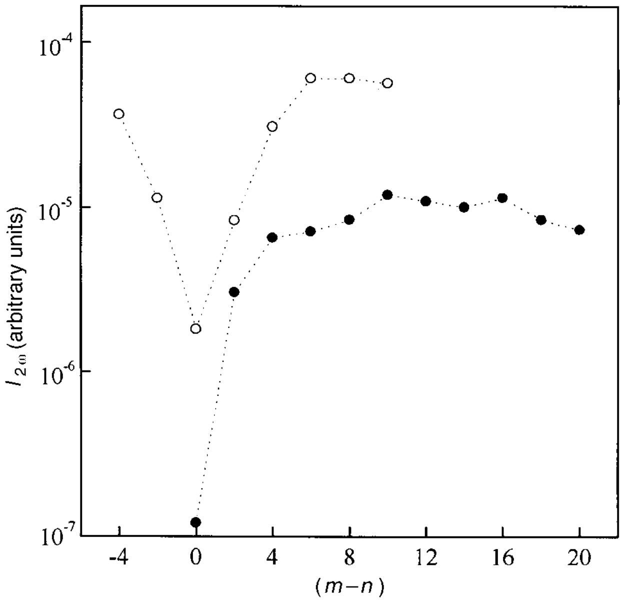
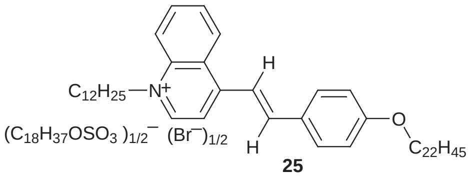


Fig. 8 Second-harmonic intensities from monolayer films of dye **23** ($m=18$; open circles) and **24** ($m=22$; filled circles) *versus* $(m-n)$, the difference in the number of carbons in the two alkyl chains.

control the deposition to fabricate $\chi^{(2)}$-inverted waveguide structures.

The above dyes form stable Z-type structures and the second-harmonic intensity increases quadratically with the number of layers.[29] This is a common feature of chromophores with hydrophobic end groups[28–34] and, unlike conventional single-legged dyes, results from the fact that the film surface is invariably hydrophobic. Included among the other examples are the quinolinium analogues, **25** and **26**, which show improved deposition characteristics and quadratic SHG enhancement to in excess of 100 layers.[31,32] The susceptibility, chromophore tilt and film thickness of **25** are as follows: $\chi_{zzz}^{(2)}=26$ pm V^{-1} at 1.064 µm, $\varphi=30°$ and $l=5.0$ nm layer^{-1}. For comparison, the length of the two-legged molecule is 5.6 nm if stretched and 3 nm if U-shaped. Thus, allowing for a slight tilt, the layer thickness is clearly in agreement with the former. The corresponding results for **26** ($n=22$, $m=12$), co-deposited with octadecanoic acid, are $\chi_{zzz}^{(2)}=35$ pm V^{-1} at 1.064 nm, $\varphi=37°$ and $l=4.3$ nm layer^{-1}, the Z-type films having a band at 470 nm and an absorbance of 1.4×10^{-3} layer^{-1} at the harmonic wavelength. In contrast, for dye **25**, the maximum is blue-shifted to 410 nm and the absorbance at 532 nm, 3×10^{-4} layer^{-1}, is slight. Furthermore, the normalised intensity, $I_{2\omega(N)}/N^2$, is comparable with the resonantly enhanced signals obtained for the hemicyanine derivatives (**2**)[80–82] but the susceptibility is lessened because the two hydrophobic chains increase the layer thickness.

This may be overcome if the alkyl groups of adjacent layers interlock. Thus, when the wide-bodied chromophore of dye **26** is substituted with alkyl groups of similar length ($n=16$, $m=18$) the LB film structure is the molecular equivalent of a zip fastener or Lego structure (Fig. 9).[125] The layer thickness and chromophore tilt angle are 2.5 nm and 38° respectively. These may be compared with 4.3 nm and 37° when the two alkyl groups are dissimilar, *i.e.* docosyl and dodecyl, the combined number of methylene groups being 34 in each case. It is important to conserve a high density of the active component in the films, the chromophore depth being 40% of the thickness in the interlocking arrangement compared with 23% in films of the isomeric analogue. However, the susceptibility is only 30 pm V^{-1} (*cf.* 35 pm V^{-1} for the non-interlocking films) because the chromophores are not optimally aligned. The number of methylene groups in the two alkyl chains should differ by at least four (see Fig. 8) whereas in this case the difference is only two. Nonetheless, the ability to simultaneously interdigitate and partially align in a Z-type manner is an important new development in the fabrication of non-centrosymmetric film structures.



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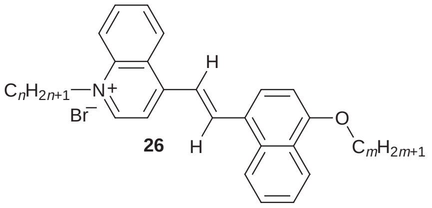

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For improved performance it is necessary to reduce the alkyl chain lengths and this has been achieved using dyes **27** to **29**. They form stable Z-type structures[33,34] (Fig. 10) because the dibutylamino group is sufficiently hydrophobic and, for all three derivatives, the SHG has remained constant for periods in excess of four years. Dye **29** has a susceptibility of $\chi_{zzz}^{(2)}=$ 26 pm V^{-1} at 1.064 µm [ref. 33(*a*)] but, when co-deposited with octadecanoic acid, Z-type deposition is improved and altered local field effects cause the value to be enhanced.[34] The films are transparent at the fundamental wavelength and have

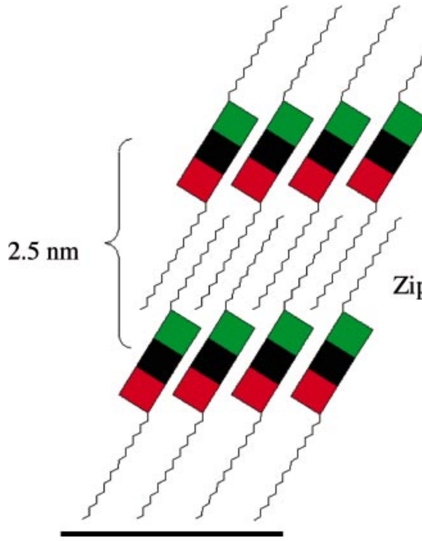


Fig. 9 Schematic representation of an interlocking Z-type arrangement of **26** ($n=16$, $m=18$), a wide-bodied chromophore with alkyl groups at opposite ends.

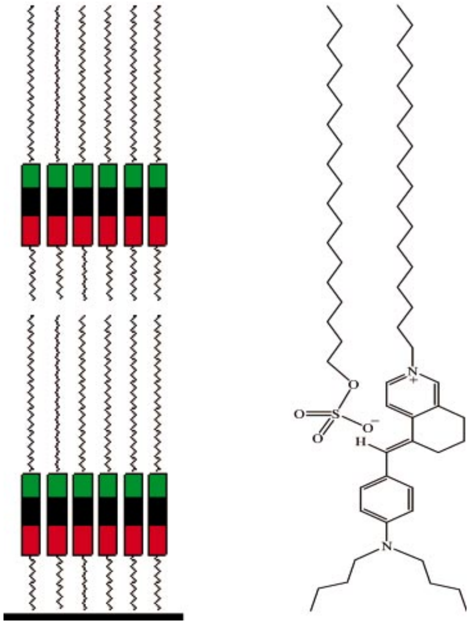
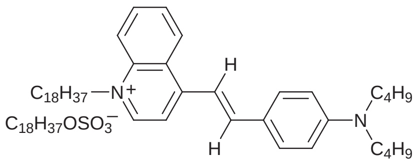
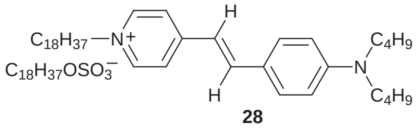


Fig. 10 Schematic representation of a Z-type structure with hydrophobic interfaces and the molecular structure of a representative dye.



27



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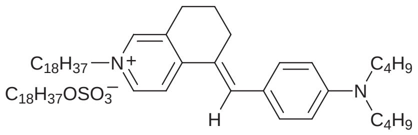

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a very slight absorbance of 5×10^{-4} layer^{-1} at 532 nm. Nonetheless, they have a high susceptibility of 76 pm V^{-1} at 1.064 µm for $\varphi=33°$ and $l=3.2$ nm layer^{-1} and, in addition, exhibit quadratic SHG enhancement to thicknesses in excess of 200 Z-type layers (Fig. 11).

Cerenkov-type SHG-active waveguides have been investigated for dye **27** using fibre optic coupling.[47] A modified deposition technique,[126] which isolates the substrate from the floating monolayer on the downstroke but allows transfer on the up-stroke, has permitted Z-type deposition on 1 µm diameter single mode optical fibre.[47] In the only previous study, Selfridge *et al.*[48] demonstrated SHG in LB overlays of a hemicyanine (dye **2**: C_nH_{2n+1}=docosyl; X^-=bromide) deposited cylindrically about a thick (600 µm core diameter) multimode fibre. Only a small proportion of the coupled pump power was guided in propagating fibre modes phase matched to the LB overlay and, therefore, a low conversion efficiency was obtained. Furthermore, transfer ratios of *ca.* 90% on the upstroke and less than 5% on the downstroke[48] resulted in an incomplete Y-type arrangement or disordered Z-type structure and, thus, the hemicyanine film was not ideally suitable. In contrast, the new materials[28–34] in conjunction with a modified deposition technique,[126] readily provide non-centrosymmetric overlays on single mode optical fibre. Also, with thickness control to *ca.* ±3 nm for dyes **27** to **29**, the overlay waveguide characteristics can be defined such that phase matching occurs at the pump wavelength.

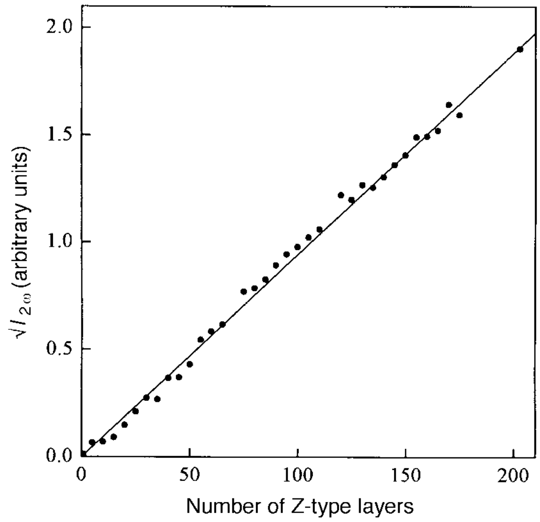

Fig. 11 Variation of the square root of the second-harmonic intensity with the number of Z-type layers of mixed films of dye **29** and octadecanoic acid (1 : 1 mole ratio).

A Cerenkov-type configuration, whereby light guided by the fibre is evanescently coupled into the LB waveguide, is depicted in Fig. 12. The second-harmonic, generated within the film, radiates into the area surrounding the overlay and, for dye **27**, is shown as a green streak in Fig. 13. An important feature of this dye, as well as its analogues above, is that both X-type and Z-type structures may be obtained by altering the direction of deposition, *i.e.* downstroke and upstroke respectively. The materials are ideal candidates for use in waveguide structures with inversion of the susceptibility in the thickness direction and, as demonstrated for DCANP,[40,41] improved conversion efficiencies should result. Furthermore, the fibre-optic device may be preferable to conventional LB waveguides where

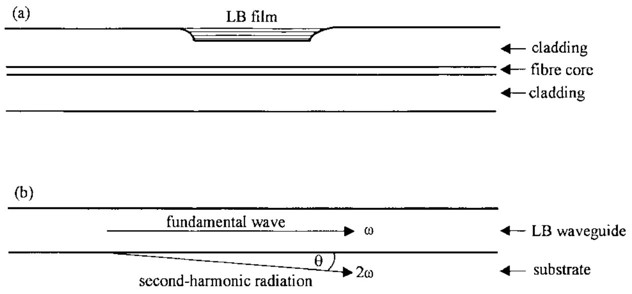

Fig. 12 Schematic diagrams of (a) the fibre optic device and (b) the Cerenkov configuration. The second-harmonic, generated in the LB waveguide, radiates into the area surrounding the film and for Cerenkov-type phase matching, the effective refractive index of the guided fundamental wave in the LB film should be greater (less) than the substrate's index at ω (2ω).

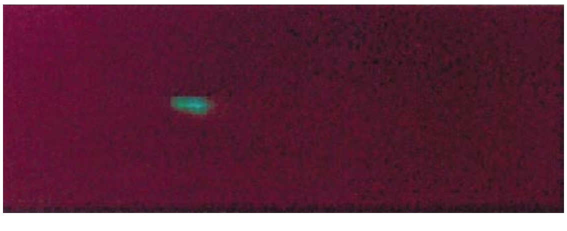

Fig. 13 Photograph of Cerenkov-type SHG (green streak) from a Z-type LB overlay of dye **27** on 1 µm diameter monomode optical fibre.[47]

prism coupling can damage the organic overlay and gratings frequently suffer from a low coupling efficiency.

8. Conclusion

In the sixteen years since SHG from an LB film was first reported, improved molecular design and modified deposition techniques have resulted in quadratic SHG enhancement to more than 100 active layers for Y-type herringbone arrangements,[13,17] alternate-layer structures[20–27] and, more recently, Z-type films in which the interface is invariably hydrophobic.[28–34] Many exhibit stable SHG at ambient temperature, in excess of four years for some of the Z-type films, and non-centrosymmetric deposition is achievable for a variety of different materials. However, to optimise the conversion efficiencies, it is necessary to eliminate inert regions of the film occupied by inactive spacers and/or the alkyl chains. Relevant to this objective, Watakabe *et al.*[116] have demonstrated non-centrosymmetric alignment of a π-conjugated oligomer with no alkyl tail (**20**). It has a weak second-order susceptibility but, nonetheless, the quadratic SHG dependence indicates that the π-electron bridge of an optically nonlinear chromophore may be utilised as the hydrophobic component for alignment at the air/water interface. It provides valuable insight into the design of appropriate D–π–A chromophores for LB deposition and illustrates a method for achieving improved properties for future nonlinear optical applications.

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References

1 (*a*) *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987; (*b*) P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley & Sons, New York, 1991; (*c*) *Optical Nonlinearities in Chemistry*, ed. J. Michl, *Chem. Rev.*, **94**, 1994; (*d*) C. Bosshard, K. Sutter, P. Pretre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, *Organic Nonlinear Optical Materials*, Gordon and Breach, Basel, 1995.

2 G. J. Ashwell, G. Jefferies, D. G. Hamilton, D. E. Lynch, M. P. S. Roberts, G. S. Bahra and C. R. Brown, *Nature*, 1995, **375**, 385.

3 G. J. Ashwell, M. P. S. Roberts, N. D. Rees, G. S. Bahra and C. R. Brown, *Langmuir*, 1998, **14**, 5279.

4 A. Dulcic, C. Flytzanis, C. L. Tang, D. Pépin, M. Fétizon and Y. Hoppilliard, *J. Chem. Phys.*, 1981, **74**, 1559.

5 R. A. Huijts and G. L. J. Hesselink, *Chem. Phys. Lett.*, 1989, **156**, 209.

6 I. Ledoux, J. Zyss, A. Jutand and C. Amatore, *Chem. Phys.*, 1991, **150**, 177.

7 A. Dulcic and C. Sauteret, *J. Chem. Phys.*, 1978, **69**, 3453.

8 S. R. Marder, D. N. Beratan and L.-T. Cheng, *Science*, 1991, **252**, 103.

9 D. J. Williams, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 690.

10 S. R. Marder and J. W. Perry, *Adv. Mater.*, 1993, **5**, 804.

11 J. F. Nicoud and R. J. Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987.

12 K. D. Singer, S. L. Lalama, J. E. Sohn and R. D. Small, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987.

13 (*a*) G. Decher, B. Tieke, C. Bosshard and P. Günter, *J. Chem. Soc., Chem. Commun.*, 1988, 933; (*b*) C. Bosshard, G. Decher, B. Tieke and P. Günter, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1988, **1017**, 141.

14 (*a*) Q. Tang, S. A. Zahir, C. Bosshard, M. Flörsheimer, M. Küpfer and P. Günter, *Thin Solid Films*, 1992, **210–211**, 195; (*b*) M. Küpfer, M. Flörsheimer, W. Baumann, C. Bosshard and P. Günter, *Spec. Publ. R. Soc. Chem.*, 1993, **137**, 74.

15 G. Decher, B. Tieke, C. Bosshard and P. Günter, *Ferroelectrics*, 1989, **91**, 193.

16 V.A. Howarth, N. Asai, N. Kishi and I. Fujiwara, *Appl. Phys. Lett.*, 1992, **61**, 1616.

17 (*a*) Y. Miyamoto, K. Kaifu, T. Koyano, M. Saito and M. Kato, *Jpn. J. Appl. Phys.*, 1991, **30**, L1647; (*b*) K. Kaifu, Y. Miyamoto, M. Saito and K. Masakazu, *J. Photopolym. Sci. Technol.*, 1993, **6**, 189.

18 (*a*) W. M. K. P. Wijekoon, B. Asgharian, P. N. Prasad, T. Geisler and S. Rosenkilde, *Thin Solid Films*, 1992, **208**, 137; (*b*) T. Geisler, S. Rosenkilde, P. S. Ramanujam, W. M. K. P. Wijekoon and P. N. Prasad, *Phys. Scr.*, 1992, **46**, 127.

19 (*a*) H. Nakahara, W. Liang, H. Kimura, T. Wada and H. Sasabe, *J. Opt. Soc. Am. B*, 1998, **15**, 458; (*b*) W. Liang, H. Nakahara, H. Kimura, T. Wada and H. Sasabe, *Thin Solid Films*, 1998, **327–329**, 423.

20 (*a*) G. J. Ashwell, E. J. C. Dawnay, A. P. Kuczynski and P. J. Martin, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1991, **1361**, 589; (*b*) G. J. Ashwell, *Spec. Publ. R. Soc. Chem.*, 1993, **137**, 31.

21 (*a*) S. Ma, K. Han, X. Lu, W. Wang, Z. Zhang and Z. Yao, *Opt. Commun.*, 1994, **111**, 513; (*b*) S. Ma, X. Lu, J. Xu, W. Wang and Z. Zhang, *J. Phys. D*, 1997, **30**, 2651.

22 G. J. Ashwell, P. D. Jackson, D. Lochun, P. A. Thompson, W. A. Crossland, G. S. Bahra, C. R. Brown and C. Jasper, *Proc. R. Soc. London A*, 1994, **445**, 385.

23 P. Hodge, Z. Ali-Adib, D. West and T. King, *Macromolecules*, 1993, **26**, 1789.

24 P. Hodge, Z. Ali-Adib, D. West and T. King, *Thin Solid Films*, 1994, **244**, 1007.

25 G. Wang, J. Wen, X. Lu, L. Liu, W. Wang, Y. Huang, H. Al, Y. Fang and F. Tao, *J. Phys. D*, 1995, **28**, 2113.

26 I. Cabrera, A. Mayer, D. Lupo, U. Falk, U. Scheunemann and W. Hickel, *Nonlinear Opt.*, 1995, **9**, 161.

27 (*a*) M. Era, K. Nakamura, T. Tsutsui, S. Saito, H. Niino, K. Takehara, K. Isomura and H. Tanaguchi, *Jpn. J. Appl. Phys.*, 1990, **29**, L2261; (*b*) M. Era, H. Kawafuji, T. Tsutsui, S. Saito, K. Takehara, K. Takehara, K. Isomura and H. Taniguchi, *Thin Solid Films*, 1992, **210–211**, 163.

28 G. J. Ashwell, P. D. Jackson and W. A. Crossland, *Nature*, 1994, **368**, 438.

29 (*a*) G. J. Ashwell, P. D. Jackson and C. Jasper, *Nonlinear Opt.*, 1995, **14**, 121; (*b*) G. J. Ashwell, P. D. Jackson, G. Jefferies, I. R. Gentle and C. H. L Kennard, *J. Mater. Chem.*, 1996, **6**, 137.

30 G. J. Ashwell, D. Lochun, I. R. Gentle, C. H. L. Kennard, G. S. Bahra and C. R. Brown, *Supramol. Sci.*, 1995, **2**, 131.

31 G. J. Ashwell, T. Handa and R. Ranjan, *J. Opt. Soc. Am.B*, 1998, **15**, 466.

32 G. J. Ashwell, D. Zhou and K. Skjonnemand, *Mol. Cryst. Liq. Cryst.*, in the press.

33 (*a*) G. J. Ashwell, G. Jefferies, C. D. George, R. Ranjan, R. B. Charters and R. P. Tatam, *J. Mater. Chem.*, 1996, **6**, 131; (*b*) G. J. Ashwell, G. Jefferies and R. Ranjan, *Electron. Lett.*, 1996, **32**, 59.

34 G. J. Ashwell and R. Ranjan, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1998, **3474**, 76.

35 C. W. Pitt and L. M. Walpita, *Thin Solid Films*, 1980, **68**, 101.

36 (*a*) C. Bosshard, M. Küpfer, P. Günter, C. Pasquier, S. Zahir and M. Siefert, *Appl. Phys. Lett.*, 1990, **56**, 1204; (*b*) C. Bosshard, M. Küpfer, M. Flörsheimer, P. Günter, C. Pasquier, S. Zahir and M. Siefert, *Makromol. Chem.-Macromol. Symp.*, 1991, **46**, 27.

37 (*a*) C. Bosshard, M. Flörsheimer, M. Küpfer and P. Günter, *Opt. Commun.*, 1991, **85**, 247; (*b*) M. Flörsheimer, M. Küpfer, C. Bosshard and P. Günter, in *Nonlinear Optics: Fundamentals, Materials and Devices*, *Proc. 5th Toyota Conf. Nonlinear Opt.*, ed. S. Miyata, Elsevier, Amsterdam, 1992, 255.

38 (*a*) M. Flörsheimer, M. Küpfer, C. Bosshard, H. Looser and P. Günter, *Adv. Mater.*, 1992, **4**, 795; (*b*) M. Küpfer, M. Flörsheimer, C. Bosshard, H. Looser and P. Günter, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1993, **1775**, 340.

39 C. Bosshard, A. Otomo, G. I. Stegeman, M. Küpfer, M. Flörsheimer and P. Günter, *Appl. Phys. Lett.*, 1994, **64**, 2076.

40 (*a*) M. Küpfer, M. Flörsheimer, C. Bosshard and P. Günter, *Electron. Lett.*, 1993, **29**, 2033; (*b*) M. Küpfer, M. Flörsheimer, C. Bosshard and P. Günter, *Nonlinear Opt.*, 1995, **10**, 341.

41 (*a*) N. Asai, H. Tamada, I. Fujiwara and J. Seto, *J. Appl. Phys.*, 1992, **10**, 4521; (*b*) I. Fujiwara, N. Asai and V. Howarth, *Thin Solid Films*, 1992, **221**, 285; (*c*) N. Asai, I. Fujiwara, H. Tamada and J. Seto, *Mater. Res. Soc. Symp. Proc.*, 1994, **328**, 91.

42 (*a*) T. L. Penner, H. R. Motschmann, N. J. Armstrong, M. C. Ezenyilimba and D. J. Williams, *Nature*, 1994, **367**, 49; (*b*) K. Clays, N. J. Armstrong, M. C. Ezenyilimba and T. L. Penner, *Chem. Mater.*, 1993, **5**, 1032.

43 (*a*) T. L. Penner, N. J. Armstrong, C. S. Willand, J. S. Schildkraut and D. R. Robello, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1991, **1560**, 377; (*b*) K. Clays, T. L. Penner, N. J. Armstrong and D. R. Robello, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1992, **1775**, 326; (*c*) T. L. Penner, N. J. Armstrong, C. S. Willand, J. S. Schildkraut, D. R. Robello and A. Ulman, *Nonlinear Opt.*, 1993, **4**, 191; (*d*) K. Clays, N. J. Armstrong and T. L. Penner, *J. Opt. Soc. Am. B*, 1993, **10**, 886.

44 (*a*) W. Hickel, B. Menges, O. Althoff, D. Lupo, U. Falk and U. Scheunemann, *Thin Solid Films*, 1994, **244**, 966; (*b*) W. Hickel, J. Bauer, D. Lupo, B. Menzel, U. Falk and U. Scheunemann, *Spec. Publ. R. Soc. Chem.*, 1993, **137**, 80.

45 S. Fujita, T. Watanabe, K. Shigehara and S. Miyata, *Nonlinear Opt.*, 1996, **15**, 493.

46 D. M. Nguyen, T. M. Mayer, S. F. Hubbard, K. D. Singer, J. A. Mann and J. B. Lando, *Macromolecules*, 1997, **30**, 6150.

47 S. S. Johal, S. W. James, R. P. Tatam and G. J. Ashwell, *Opt. Lett.*, in the press.

48 (*a*) R. H. Selfridge, S. T. Kowel, P. Stroeve, J. Y. S. Lam and B. G. Higgins, *Thin Solid Films*, 1988, **160**, 471; (*b*) R. H. Selfridge, T. K. Moon, P. Stroeve, J. Y. S. Lam, S. T. Kowel and A. Knoesen, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1988, **971**, 197.

49 (*a*) G. J. Ashwell, E. J. C. Dawnay, A. P. Kuczynski, M. Szablewski, I. M. Sandy, M. R. Bryce, A. M. Grainger and M. Hasan, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1117; (*b*) G. J. Ashwell, G. Jefferies, E. J. C. Dawnay, A. P. Kuczynski, D. E. Lynch, G. Yu and D. G. Bucknall, *J. Mater. Chem.*, 1995, **5**, 975.

50 (*a*) M. A. Rutkis, E. Wistus, S. E. Lindquist, E. Mukhtar, G. Liberts, V. Zauls, A. B. Klimkans and E. A. Silinsh, *Adv. Mater. Opt. Electron.*, 1996, **6**, 39; (*b*) E. A. Silinsh, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1997, **2968**, 24; (*c*) G. Liberts, V. Zauls and N. Ojars, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1997, **2968**, 19.

51 F. Grunfeld, *Rev. Sci. Instrum.*, 1993, **64**, 548.

52 G. J. Ashwell, G. S. Bahra, C. R. Brown, D. G. Hamilton, C. H. L. Kennard and D. E. Lynch, *J. Mater. Chem.*, 1996, **6**, 23.

53 J. Bernstein and E. Goldstein, *Mol. Cryst. Liq. Cryst.*, 1988, **164**, 213.

54 C. W. Dirk, W. C. Herndon, F. Cervantes-Lee, H. Selnau, S. Martinez, P. Kalamegham, A. Tan, G. Campos, M. Velez, J. Zyss, I. Ledoux and L.-T. Cheng, *J. Am. Chem. Soc.*, 1995, **117**, 2214.

55 G. J. Ashwell, P. C. Williamson, G. S. Bahra and C. R. Brown, *Aust. J. Chem.*, **1999**, **52**, 37.

56 G. J. Ashwell, G. M. S. Wong, D. G. Bucknall, G. S. Bahra and C. R. Brown, *Langmuir*, 1997, **13**, 1629.

57 G. J. Ashwell, A. N. Dyer and A. Green, *Langmuir*, 1999, **15**, 3627.

58 (*a*) J.-L. Brédas and E. Brouyère, private communication; (*b*) E. Brouyère, PhD Thesis, Université de Mons-Hainaut, 1997.

59 C. L. Honeybourne, *J. Mater. Chem.*, 1999, 2241.

60 H. Chen, W. G. Herkstroeter, J. Perlstein, K. Y. Law and D. G. Whitten, *J. Phys. Chem.*, 1994, **98**, 5138.

61 G. J. Ashwell, G. Jefferies, N. D. Rees, P. C. Williamson, G. S. Bahra and C. R. Brown, *Langmuir*, 1998, **14**, 2850.

62 G. J. Ashwell, *J. Mater. Chem.*, 1998, **8**, 373.

63 G. J. Ashwell, P. Leeson, G. S. Bahra and C. R. Brown, *J. Opt. Soc. Am. B*, 1998, **15**, 484.

64 G. J. Ashwell, P. C. Williamson, A. Green, G. S. Bahra and C. R. Brown, *Aust. J. Chem.*, 1998, **51**, 599.

65 H. Chen, K. Y. Law and D. G. Whitten, *J. Phys. Chem.*, 1996, **100**, 5949.

66 (*a*) T. Bjørnholm, T. Geisler, J. Larsen, M. Jørgensen, *J. Chem. Soc., Chem. Commun.*, 1992, 815; (*b*) T. Bjørnholm, T. Geisler, J. Larsen, M. Jørgensen, K. Brunfeldt, K. Schaumburg and K. Bechgaard, *Synth. Met.*, 1993, **57**, 3813; (*c*) T. Geisler and T. Bjørnholm, *Synth. Met.*, 1993, **57**, 3842.

67 (*a*) D. B. Neal, M. C. Petty, G. G. Roberts, M. M. Ahmad, W. J. Feast, I. R. Girling, N. A. Cade, P. V. Kolinski and I. R. Peterson, *Electron. Lett.*, 1986, **22**, 460; (*b*) D. B. Neal, M. C. Petty, G. G. Roberts, M. M. Ahmad, W. J. Feast, I. R. Girling, N. A. Cade, P. V. Kolinski and I. R. Peterson, *Proc. 6th IEEE Int. Symp. Appl. Ferroelectr.*, 1986, 89.

68 G. J. Ashwell, D. Zhou, K. Skjonnemand, R. Ranjan, C. Huang and T. Cheng, *Langmuir*, in the press.

69 S. Allen, T. McLean, P. F. Gordon, B. D. Bothwell, P. Robin and I. Ledoux, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1988, **971**, 206.

70 I. Ledoux, D. Josse, P. Fremaux, J.-P. Piel, G. Post, J. Zyss, T. McLean, R. A. Hann, P. F. Gordon and S. Allen, *Thin Solid Films*, 1988, **160**, 217.

71 (*a*) R. M. Swart, E. S. Froggatt, A. N. Burgess, A. Eaglesham, D. P. Devonald, M. G. Hutchins, S. Allen and T. G. Ryan, *Thin Solid Films*, 1992, **210–211**, 237; (*b*) J. P. Cresswell, M. C. Petty, J. E. Shearman, S. Allen, T. G. Ryan and I. Ferguson, *Thin Solid Films*, 1994, **244**, 1067; (c) C. H. Wang, B.S. Wherrett, J. P. Cresswell, M. C. Petty, T. G. Ryan, S. Allen, I. Ferguson, M. G. Hutchins and D. P. Devonald, *Opt. Lett.*, 1995, **14**, 1533; (*d*) J. P. Cresswell, M. C. Petty, I. Ferguson, M. G. Hutchins, S. Allen, T. G. Ryan, C. H. Wang and B. S. Wherrett, *Adv. Mater. Opt. Electron.*, 1996, **6**, 33.

72 (*a*) R. C. Hall, G. A. Lindsay, B. L. Anderson, S. T. Kowel, B. G. Higgins and P. Stroeve, *Mater. Res. Soc. Symp. Proc.*, 1988, **109**, 351; (*b*) B. L. Anderson, R. C. Hall, B. G. Higgins, G. A. Lindsay, P. Stroeve and S. T. Kowell, *Synth. Met.*, 1989, **28**, D683.

73 M. J. Roberts, G. A. Lindsay, K. J. Wynne, R. A. Hollins, P. Zarras, J. D. Stenger-Smith, M. Nadler and A. P. Chafin, *Polym. Prepr.*, 1997, **38**, 975.

74 H. R. Motschmann, T. L. Penner, N. J. Armstrong and M. C. Ezenyilimba, *J. Phys. Chem.*, 1993, **97**, 3933.

75 W. M. K. P. Wijekoon, S. K. Wijaya, J. D. Bhawalkar, P. N. Prasad, T. L. Penner, N. J. Armstrong, M. C. Ezenyilimba and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4480.

76 (*a*) G. A. Lindsay, K. J. Wynne, W. N. Herman, A. P. Chafin, R. A. Hollins, J. D. Stenger-Smith, J. Hoover, J. Cline and M. J. Roberts, *Nonlinear Opt.*, 1996, **15**, 139; (*b*) G. A. Lindsay, M. J. Roberts, J. D. Stenger-Smith, W. N. Herman, P. R. Ashley and K. J. Wynne, *Nav. Res. Rev.*, 1997, **XLIX**, 21; (*c*) W. N. Herman, M. J. Roberts, J. D. Stenger-Smith, A. P. Chafin, R. A. Hollins, G. A. Lindsay and K. J. Wynne, *Polym. Prepr.*, 1998, **39**, 1105.

77 G. J. Ashwell, R. C. Hargreaves, C. E. Baldwin, G. S. Bahra and C. R. Brown, *Nature*, 1992, **357**, 393.

78 M. C. J. Young, R. Jones, R. H. Tredgold, W. X. Lu, Z. Ali-Adib, P. Hodge and F. Abbasi, *Thin Solid Films*, 1989, **182**, 319.

79 X. Liu, L. Liu, Z. Chen, X. Lu, J. Zheng and W. Wang, *Thin Solid Films*, 1992, **219**, 221.

80 I. R. Girling, N. A. Cade, P. V. Kolinski, R. J. Jones, I. R. Peterson, M. M. Ahmad, D. B. Neal, M. C. Petty, G. G. Roberts and W. J. Feast, *J. Opt. Soc. Am. B*, 1987, **4**, 950.

81 L. M. Hayden, *Phys. Rev. B*, 1988, **38**, 3718.

82 (*a*) J. S. Schildkraut, T. L. Penner, C. S. Willand and A. Ulman, *Opt. Lett.*, 1988, **13**, 134; (*b*) M. A. Carpenter, C. S. Willand, T. L. Penner, D. J. Williams and S. Mukamel, *J. Phys. Chem.*, 1992, **96**, 2801.

83 G. J. Ashwell, T. W. Walker, I. R. Gentle, G. Foran, G. S. Bahra and C. R. Brown, *J. Mater. Chem.*, 1996, **6**, 969.

84 F. Davis, P. Hodge, X.-H. Liu and Z. Ali-Adib, *Macromolecules*, 1994, **27**, 1957.

85 K. Han, X. Lu, J. Xu, S. Ma and W. Wang, *Opt. Commun.*, 1998, **152**, 371.

86 L. M. Hayden, B. L. Anderson, J. Y. S. Lam, B. G. Higgins, P. Stroeve and S. T. Kowell, *Thin Solid Films*, 1988, **160**, 379.

87 L. Liu, J. Zheng, W. Wang, Z. Zhang, F. Tao, L. Xu and J. Hu, *Opt. Commun.*, 1992, **93**, 207.

88 D. Dunne, P. Hodge, Z. Ali-Adib, N. B. McKeown and D. West, *J. Mater. Chem.*, 1998, **8**, 1391.

89 (*a*) B. L. Anderson, J. M. Hoover, G. A. Lindsay, B. G. Higgins, P. Stroeve and S. T. Kowel, *Thin Solid Films*, 1989, **179**, 413; (*b*) R. C. Hall, G. A. Lindsay, S. T. Kowel, L. M. Hayden, B. L. Anderson, B. G. Higgins, P. Stroeve and M. P. Srinivasan, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1987, **824**, 121.

90 (*a*) M. C. J. Young, W. X. Lu, R. H. Tredgold, P. Hodge and F. Abbasi, *Electron. Lett.*, 1990, **26**, 993; (*b*) M. Bardosova, F. Davis, R. H. Tredgold, Z. Ali-Adib, B. Hunt and V. Shmatko, *Thin Solid Films*, 1994, **244**, 740.

91 J. P. Cresswell, M. C. Petty, C. H. Wang, B. S. Wherrett, Z. Ali-Adib, P. Hodge, T. G. Ryan and S. Allen, *Opt. Commun.*, 1995, **115**, 271.

92 G. J. Ashwell, K. R. Ranjan, A. J. Whittam and D. Gandolfo, *J. Mater. Chem.*, in the press.

93 J. F. McGilp, Z. R. Tang and M. Cavanagh, *Synth. Met.*, 1993, **61**, 181.

94 G. J. Ashwell and A. J. Whittam, *Mol. Cryst. Liq. Cryst.*, in the press.

95 G. J. Ashwell, T. W. Walker, P. Leeson, U.-W. Grummt and F. Lehmann, *Langmuir*, 1998, **14**, 1525.

96 M. A. Schoondorp, A. J. Schouten, J. B. E. Hulshof and B. L. Feringa, *Langmuir*, 1993, **9**, 1323.

97 S. Allen, T. G. Ryan, D. P. Devonald, M. G. Hutchings, A. N. Burgess, E. S. Froggatt, A. Eaglesham, R. M. Swart, G. J. Ashwell and M. Malhotra, *Spec. Publ. R. Soc. Chem.*, 1991, **91**, 51.

98 (*a*) M. Conroy, Z. Ali-Adib, P. Hodge, D. West and T. King, *J. Mater. Chem.*, 1994, **4**, 1; (*b*) D. West, D. Dunne, P. Hodge, N.B. McKeown and Z. Ali-Adib, *Thin Solid Films*, 1998, **323**, 227.
99 R. H. Tredgold, M. C. J. Young, R. Jones, P. Hodge, P. Kolinski and R. J. Jones, *Electron. Lett.*, 1988, **24**, 308.
100 Y. Liu, Y. Xu, D. Zhu, T. Wada, H. Sasabe, X. Zhao and X. Xie, *J. Phys. Chem.*, 1995, **99**, 6957.
101 (*a*) H. Sakaguchi, H. Nakamura, T. Nagamura, T. Ogawa and T. Matsuo, *Chem. Lett.*, 1989, 1715; (*b*) H. Sakaguchi, T. Nagamura, T.L. Penner and D.G. Whitten, *Thin Solid Films*, 1994, **244**, 947.
102 H. Hsiung, J. Rodriguez-Parada and R. Beckerbauer, *Chem. Phys. Lett.*, 1991, **182**, 88.
103 C. Bubeck, A. Laschewsky, D. Lupo, D. Neher, P. Ottenbreit, W. Paulus, W. Prass, H. Ringsdorf and G. Wegner, *Adv. Mater*, 1991, **3**, 54.
104 O. A. Aktsipetrov, E. D. Mishina, T. V. Misuryaev, A. A. Nikulin, V. R. Novak, R. Stolle and T. Rasing, *Surf. Sci.*, 1998, **402–404**, 576.
105 M. J. Roberts, G. A. Lindsay, J. D. Stenger-Smith, R. A. Hollins, A. P. Chafin and R. G. Gratz, *Thin Solid Films*, 1998, **327–329**, 5.
106 (*a*) R. Popovitz-Biro, K. Hill, E. M. Landau, M. Lahav, L. Lieserowitz, J. Sagiv, H. Hsiung, G. R. Meredith and H. Vanherzeele, *J. Am. Chem. Soc.*, 1988, **110**, 2672; (*b*) R. Popovitz-Biro, K. Hill, E. Shavit, M. Lahav, L. Lieserowitz, J. Sagiv, H. Hsiung, G. R. Meredith and H. Vanherzeele, *J. Am. Chem. Soc.*, 1990, **112**, 2498.
107 T. Richardson, G. G. Roberts, M. E. C. Polywka and S. G. Davies, *Thin Solid Films*, 1988, **160**, 231.
108 T. Senoh, K. Sanui and N. Ogata, *Chem. Lett.*, 1990, 1849.
109 L. M. Hayden, S. T. Kowel and M. P. Srinivasan, *Opt. Commun.*, 1987, **61**, 351.
110 I. Ledoux, D. Josse, P. Vidakovic, J. Zyss, R. A. Hann, P. F. Gordon, B. D. Bothwell, S. K. Gupta, S. Allen, P. Robin, E. Chastaing and J.-C. Dubois, *Europhys. Lett.*, 1987, **3**, 803.
111 N. Kalita, J. P. Cresswell, M. C. Petty, A. McRoberts, D. Lacey, G. Gray, M.J. Goodwin and N. Carr, *Opt. Mater.*, 1992, **1**, 259.
112 K. Isomura, K. Takehara, K. Kobayashi, G. Funakoshi, H. Taniguchi, M. Era, T. Tsutsui and S. Saito, *Thin Solid Films*, 1994, **244**, 939.
113 Y. Liu, Y. Xu, D. Zhu, T. Wada, H. Sasabe, L. Liu and W. Wang, *Thin Solid Films*, 1994, **244**, 943.
114 D.-W. Cheong, W.-H. Kim, L. A. Samuelson, J. Kumar and S. K. Tripathy, *Macromolecules*, 1996, **29**, 1416.
115 (*a*) O. A. Aktsipetrov, N. N. Akhmediev, E. D. Mishina and V. R. Novak, *JETP Lett.*, 1983, **37**, 207; (*b*) O. A. Aktsipetrov, N. N. Akhmediev, I. M. Baranova, E. D. Mishina and V. R. Novak, *Sov. Phys. JETP (Engl. Transl.)*, 1985, **62**, 524.
116 A. Watakabe, H. Okada and T. Kunitake, *Langmuir*, 1994, **10**, 2722.
117 D.-W. Cheong, J.-I. Chen, J. Kumar and S. K. Tripathy, *Mater. Res. Soc. Symp. Proc.*, 1996, **413**, 281.
118 M. N. Teerenstra, J. G. Hagting, A. J. Schouten, R. J. M. Nolte, M. Kauranen, T. Verbiest and A. Persoons, *Macromolecules*, 1996, **29**, 4876.
119 (*a*) G. J. Ashwell, J. R. Sambles, A. S. Martin, W. G. Parker and M. Szablewski, *J. Chem. Soc., Chem. Commun.*, 1990, 1374; (*b*) A. S. Martin, J. R. Sambles and G. J. Ashwell, *Phys. Rev. Lett.*, 1993, **70**, 218.
120 R. M. Metzger, B. Chen, U. Hopfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer and G. J. Ashwell, *J. Am. Chem. Soc.*, 1997, **119**, 10455.
121 *Langmuir-Blodgett Films*, ed. G. G. Roberts, Plenum Press, New York, 1990.
122 A. Ulman, *An Introduction to Ultrathin Films: from Langmuir-Blodgett to Self-Assembly*, Academic Press, San Diego, 1991.
123 M. C. Petty, *Langmuir-Blodgett Films: an Introduction*, Cambridge University Press, Cambridge, 1996.
124 G. J. Ashwell, D. Lochun and A. N. Dyer, *Mol. Cryst. Liq. Cryst.*, in the press.
125 G. J. Ashwell, D. Zhou and K. Skjonnemand, *Langmuir*, submitted for publication.
126 S. S. Johal, S. W. James, R. P. Tatam and G. J. Ashwell, *Meas. Sci. Technol.*, 1999, **10**, N60.

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